

Study of ^1H NMR Spectra of Dinuclear Complexes of Heavy Lanthanides with Phthalocyanines Based on Separation of the Effects of Two Paramagnetic Centers

Naoto Ishikawa,* Tomochika Iino, and Youkoh Kaizu*

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

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Experimental and theoretical study of nuclear magnetic resonance (NMR) spectra of dinuclear complexes of paramagnetic trivalent Tb, Dy, Ho, Er, Tm, or Yb ions with phthalocyanine ligands is presented. The ^1H NMR paramagnetic shifts of the dinuclear Pc triple-decker complexes PcLnPcLnPc^* (abbreviated as [Ln, Ln]; Pc is the dianion of phthalocyanine and Pc^* is the dianion of 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine) were measured in CDCl_3 solution at 303 K. These values are analyzed using the corresponding data of two series of heterodinuclear complexes with a single paramagnetic ion, namely PcYPcLnPc^* ([Y, Ln]) and PcLnPcYPc^* ([Ln, Y]). The paramagnetic shifts in [Y, Ln] and [Ln, Y] were reproduced solely by the magnetic dipolar (pseudo-contact) term, using a geometric structure that was obtained by a density functional theory (DFT) calculation with a moderate modification. Each paramagnetic shift value of [Ln, Ln] is shown to be sum of those of [Y, Ln] and [Ln, Y]. The independence of the paramagnetic shift contributions of the two Ln ions is explained by the small interaction between f-electronic systems in [Ln, Ln]. The shifts in an [Ln, Ln] complex have the same sign, because all the protons are positioned in the same region of the contour map of the dipolar contributions of the two paramagnetic sites.

Introduction

Dinuclear lanthanide complexes provide rare opportunities to study the interaction between two 4f-electronic systems in an isolated environment. Typical forms of such complexes include those which have triple-helix structures of polydentate ligands that are based on benzimidazole and pyridine^{1–3} or dipicolinic acid^{4,5} and those with “triple-decker” structures of phthalocyanines,^{6,7} porphyrins,⁸ or mixtures of the latter two. In these dinuclear systems, two 4f-electronic centers are placed in close proximity, at a distance at which a sizable interaction between them is expected to exist.

From the perspective of “stacked π -conjugated molecules”, Ishikawa and Kaizu et al. reported a series of studies on the spectroscopic properties and electronic structures of the Pc triple-decker complexes (where Pc is the dianion of phthalocyanine), in terms of π – π interactions between adjacent ligands.^{9–11} Recently, the authors published two papers about experimental and theoretical studies of the 4f-electronic structures of the Pc triple deckers from the viewpoint of “multiple 4f-element systems”.^{12,13}

In the first report, the authors studied the magnetic properties and electronic structure of individual 4f-shells using newly prepared heterodinuclear complexes that are composed of a diamagnetic Y^{3+} ion and a paramagnetic trivalent lanthanide ion, PcYPcLnPc^* (abbreviated hereinafter as [Y, Ln], where Pc is as previously defined, Pc^* is the dianion of 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine, and Ln = Tb, Dy, Ho, Er, Tm, or Yb).¹² The sublevel structures of the ground states of the six [Y, Ln] that have 4f⁸ to 4f¹³ configurations were determined through finding the set of ligand-field parameters that reproduces paramagnetic shifts of ^1H NMR and temperature dependences of magnetic susceptibility.

In the subsequent report,¹³ the interactions between 4f systems in [Ln, Ln] were studied. The effects of the f–f interactions were detected as changes in the temperature dependence of magnetic susceptibility through a comparative study of [Y, Ln], PcLnPcYPc^* (abbreviated as [Ln, Y]) and homodinuclear complexes PcLnPcLnPc^* (abbreviated as [Ln, Ln]). On the basis of theoretical calculations using the ligand-field parameters determined separately for the two Ln sites, we found that the interactions between the 4f systems in [Ln, Ln] were essentially of a magnetic-dipolar nature. The characteristic temperature dependences observed in the homodinuclear systems were explained by the anisotropy in the magnetic susceptibility of the noninteracting 4f systems. The report was the first quantitative study of f–f interaction in dinuclear lanthanide complexes.

The purpose of this paper is to elucidate the origin of the paramagnetic shifts in the ^1H NMR spectra of the dinuclear lanthanide triple-decker Pc complexes. The first comprehensive study on the assignments of ^1H NMR spectra of homodinuclear Pc triple deckers was reported by Arnold and Jiang for the series of compounds formulated as $\text{PcLnPc}^{**}\text{LnPc}^{**}$ and $\text{PcLnPc}^{**}\text{LnPc}$ (where Pc^{**} is the dianion of 2,3,9,10,16,17,23,24-octa-octoxyphthalocyanine and Ln is Y, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, or Tm).¹⁴ Because no theoretical information on the f-electronic structures of the lanthanide Pc complexes was available at the time, the origin of the paramagnetic shifts was discussed using the method^{15,16} in which the terms higher than quadratic in the operator equivalent representation of the ligand-field potential are omitted and the parameter $A_2^0(r^2)$, i.e., the coefficient for the quadratic term, is assumed to be constant across the lanthanide series.¹⁷ This approximation has been shown to give a reasonably good reproduction of experimental shifts for the cases such as tris-(2,6-dipicolinato)lanthanides and tris(dipivaloylmethanato)lanthanides.^{18,19} Recently, Ouali et al. reported a successful analysis of ^1H NMR spectra of lanthanide triple-helical complexes, using

* Author to whom correspondence should be addressed. E-mail: ishikawa@chem.titech.ac.jp.

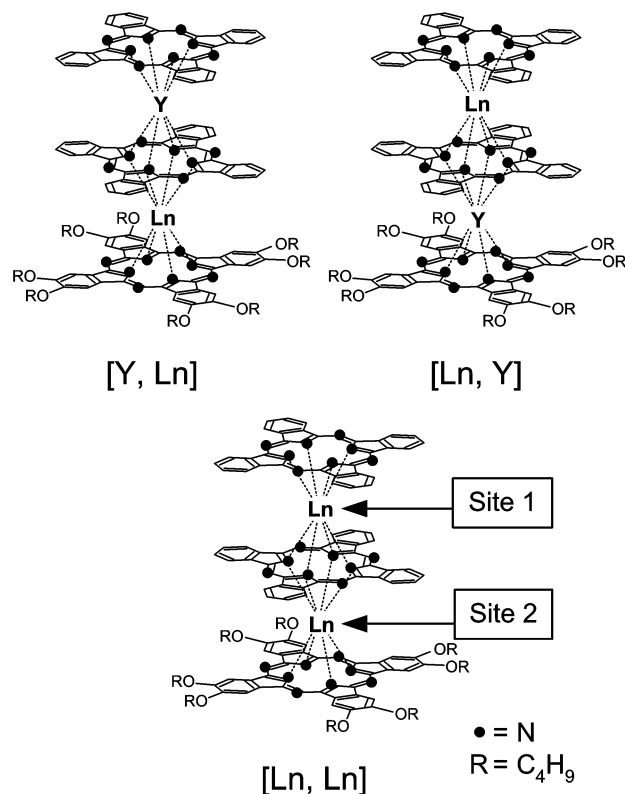


Figure 1. Schematic diagram of [Y, Ln], [Ln, Y], and [Ln, Ln] (Ln = Tb, Dy, Ho, Er, Tm, or Yb).

an extension of the method to the trinuclear systems.²⁰ In the Pc triple-decker complexes, however, the assumption used in the approach is inappropriate: our studies have shown that the $A_2^0(r^2)$ parameter is highly dependent on the atomic number of the Ln ion and the higher-order terms are not negligible.^{12,13} A different approach must be taken to discuss the origin of the shifts in the present case.

In this paper, we present the first investigation of the ^1H NMR of the homodinuclear heavy lanthanide complexes based on a separate analysis of each effect of the two paramagnetic centers on the two different sites (sites 1 and 2 in Figure 1). To determine the contributions of magnetic-dipolar and Fermi-contact terms on the paramagnetic shifts due to a single paramagnetic center, spectra of two types of the heterodinuclear complexes, [Y, Ln] and [Ln, Y], will be first examined. Next, the complexes with two paramagnetic centers, [Ln, Ln], will be discussed. We will show how the contributions from each ion and interaction between f-electronic systems determine the observed paramagnetic shifts in the dinuclear systems.

Experiments

The synthesis of [Y, Ln] (Ln = Tb, Dy, Ho, Er, Tm, or Yb) was described in ref 12, and that of [Ln, Y] and [Ln, Ln] was described in ref 13. ^1H NMR spectra of the complexes were measured in CDCl_3 solution at 30 °C on a JEOL model Lambda-300 NMR spectrometer.

Calculations

We have used two models for the geometric structures of the complexes. In the first model, which we will reference as Model 1, the Pc triple-decker portion in the complexes was determined by a density functional theory (DFT) calculation of Pc_3Y_2 using a B3LYP model²¹ and a LANL2DZ basis set^{22,23}

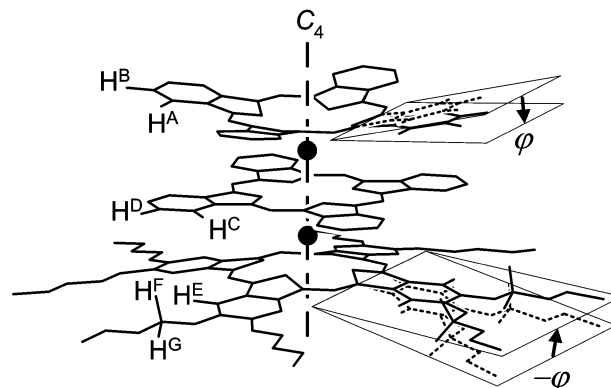


Figure 2. Notations for the protons in [Y, Ln], [Ln, Y], and [Ln, Ln]. The geometries of Model 1 and 2 are shown by dotted and solid lines, respectively.

with the Gaussian 98 program.²⁴ The geometry of the butoxy parts was estimated by superposing the optimized geometry of 1,2-dibutoxybenzene with C_{2v} symmetry, using the B3LYP/LANL2DZ model on that of Pc_3Y_2 . The calculations were performed on a NEC model SX-5 vector supercomputer at Global Scientific Information and Computing Center at the Tokyo Institute of Technology.

The structure so determined is shown in Figure 2, with the notations of the seven protons to be discussed. Because of the large molecular size of Pc_3Y_2 , the computing power required for the use of basis sets with polarization functions was prohibitive. Because of the lack of polarization functions in the basis set, the prediction of the distortion from planarity of the outer Pc ligands—and, hence, the positions of H^{A} , H^{B} , and H^{E} —are not quite accurate. In contrast, the accuracy of the positions of H^{C} and H^{D} , which belong to the planar Pc, is expected to be much better.

In Model 2, to compensate for the poor prediction of the distortion of the outer ligands, the geometry of Model 1 is modified. The isoindole moieties are bent along the line that connects the two C atoms at α -positions by an angle φ in the manner shown in Figure 2. In a later section, we will investigate how this compensation improves the agreement of the numerical prediction of the NMR paramagnetic shifts to the experimental data.

Results and Discussion

Paramagnetic Shifts in the Heterodinuclear Complexes with a Single Paramagnetic Ion. Table 1 shows the chemical shifts δ of the NMR signals of the protons in [Y, Y], [Y, Ln], [Ln, Y], and [Ln, Ln]. The signals in the diamagnetic [Y, Y] are observed at the normal regions for the protons of Pc complexes and $-\text{OCH}_2-$ protons. The signal assignments for [Y, Y] and [Y, Ln] have been performed in ref 12.

It has been shown that paramagnetic shifts (hereinafter referenced as $\Delta\delta$) of the protons in [Y, Ln] have a predominantly magnetic-dipolar nature.¹² The dipolar shift induced by a Ln ion is written as

$$\Delta\delta = \frac{\Delta\nu}{\nu} = \frac{3(\cos^2\theta) - 1}{2R^3}D \quad (1)$$

where

$$D = \chi_{zz} - \frac{\chi_{xx} + \chi_{yy} + \chi_{zz}}{3} \quad (2)$$

TABLE 1: Assignments of ^1H NMR Signals of [Y, Y], [Ln, Y], [Y, Ln], and [Ln, Ln] in CDCl_3 Solution at 303 K

	H ^A	H ^B	H ^C	H ^D	H ^E	H ^F	H ^G
[Y, Y] ^b	8.46	8.06	8.99	8.73	7.95	4.72	4.44
[Y, Tb] ^b	24.08	9.77	-65.39	-31.67	-66.69	-30.33	-20.85
[Y, Dy] ^b	16.40	8.96	-27.83	-10.94	-29.81	-12.88	-8.19
[Y, Ho] ^b	11.31	8.37	-4.27	1.81	-5.78	-1.61	-0.17
[Y, Er] ^b	4.99	7.64	25.12	17.81	24.52	12.54	10.16
[Y, Tm] ^b	3.77	7.56	31.00	20.91	31.00	15.61	12.35
[Y, Yb] ^b	7.83	7.94	11.40	10.09	10.68	6.02	5.38
[Tb, Y]	-65.12	-30.47	-68.58	-33.10	23.24	-1.52	6.49
[Dy, Y]	-29.87	-11.91	-29.32	-11.91	15.82	1.61	5.54
[Ho, Y]	-4.70	0.73	-4.50	1.76	10.68	3.64	4.83
[Er, Y]	25.16	16.05	26.23	18.35	4.49	6.09	3.95
[Tm, Y]	30.76	19.11	31.65	21.14	3.46	6.63	3.72
[Yb, Y]	10.94	9.23	11.31	10.02	7.29	4.87	4.34
[Tb, Tb]	-50.27	-29.31	-142.70	-73.38	-52.46	-37.18	-19.20
[Dy, Dy]	-22.20	-11.54	-68.50	-32.47	-22.84	-16.62	-7.45
[Ho, Ho]	-2.50	0.72	-19.50	-5.93	-3.10	-3.10	-0.20
[Er, Er]	21.80	15.72	43.00	27.77	21.00	14.04	9.74
[Tm, Tm]	26.53	18.89	55.60	34.35	26.96	17.91	11.92
[Yb, Yb]	10.49	9.23	14.26	11.68	10.22	6.30	5.35

^a All chemical-shift values (δ) are in given in units of ppm relative to TMS. ^b Data from ref 12.

TABLE 2: Paramagnetic Shifts of [Ln, Y], [Y, Ln], and [Ln, Ln]^a

	H ^A	H ^B	H ^C	H ^D	H ^E	H ^F	H ^G
[Y, Tb] ^b	15.62	1.71	-74.38	-40.40	-74.64	-35.05	-25.29
[Y, Dy] ^b	7.94	0.90	-36.82	-19.67	-37.76	-17.60	-12.63
[Y, Ho] ^b	2.85	0.31	-13.26	-6.92	-13.73	-6.33	-4.61
[Y, Er] ^b	-3.47	-0.42	16.13	9.08	16.57	7.82	5.72
[Y, Tm] ^b	-4.69	-0.50	22.01	12.18	23.05	10.89	7.91
[Y, Yb] ^b	-0.63	-0.12	2.41	1.36	2.73	1.30	0.94
[Tb, Y]	-73.58	-38.53	-77.57	-41.83	15.29	-6.24	2.05
[Dy, Y]	-38.33	-19.97	-38.31	-20.64	7.87	-3.11	1.10
[Ho, Y]	-13.16	-7.33	-13.49	-6.97	2.73	-1.08	0.39
[Er, Y]	16.70	7.99	17.24	9.62	-3.46	1.37	-0.49
[Tm, Y]	22.30	11.05	22.66	12.41	-4.49	1.91	-0.72
[Yb, Y]	2.48	1.17	2.32	1.29	-0.66	0.15	-0.10
[Tb, Tb]	-58.73	-37.37	-151.69	-82.11	-60.41	-41.90	-23.64
[Dy, Dy]	-30.66	-19.60	-77.49	-41.20	-30.79	-21.34	-11.89
[Ho, Ho]	-10.96	-7.34	-28.49	-14.66	-11.05	-7.82	-4.64
[Er, Er]	13.34	7.66	34.01	19.04	13.05	9.32	5.30
[Tm, Tm]	18.07	10.83	46.61	25.62	19.01	13.19	7.48
[Yb, Yb]	2.03	1.17	5.27	2.95	2.27	1.58	0.91

^a Paramagnetic-shift values ($\Delta\delta$) given in units of ppm. ^b Data from ref 12.

ν is the resonance frequency in the reference diamagnetic molecule, $\Delta\nu$ is the change in the frequency in the paramagnetic molecule, R is the distance between the Ln ion and the atom under consideration, and θ is the corresponding azimuth. The three principal values of magnetic moment of the Ln ion are denoted as χ_{xx} , χ_{yy} , and χ_{zz} . The z -axis coincides with the C_4 symmetric axis. Because of the axial symmetry, eq 2 is simplified as $D = 2(\chi_{zz} - \chi_{xx})/3$, which is two-thirds of the difference between the principal components parallel and perpendicular to the C_4 -axis.

The $\Delta\delta$ values are tabulated in Table 2. We use the same definition as the previous reports, that a paramagnetic shift is the deviation of a NMR signal from the corresponding signal of [Y, Y]. By inspecting the table, we can divide the protons into two groups by the signs of the shifts. In [Y, Ln], H^A and H^B have the same sign and H^C–H^G have the opposite sign. In [Ln, Y], H^A–H^D and H^F have the same sign, whereas H^E and H^G have the opposite sign.

Evidence for the predominance of the magnetic-dipolar term against the Fermi contact term in the paramagnetic shifts in [Y, Ln] can be observed in that the relative values of the shifts are constant over the six lanthanide cases.¹² Table 3 presents the

ratios of the shifts relative to that of H^C. The ratios are almost constant, not only in the [Y, Ln] set but also in the [Ln, Y] set.

There are noticeable deviations in the Yb cases from the other cases in Table 3. This distinction is ascribed to the prominently small $\Delta\delta$ values in the ytterbium complexes, as shown in Table 2. Therefore, the relative significance of the effect of the structural difference from [Y, Y] on chemical shifts is much higher than that in the other complexes.

Relation between the Positions of the Protons and the $\Delta\delta$ Values in [Y, Ln] and [Ln, Y]. Figure 3 shows the contour plot of the magnetic-dipolar term that is due the Ln ion on site 2, along with the positions of the protons of Models 1 and 2. The solid lines indicate the position θ ($\theta = \arccos[(1/3)^{1/2}] = 54.7^\circ$) across which the dipolar term changes its sign. Protons H^A and H^B in the ligand far from the Ln ion are in the region $\theta < 54.7^\circ$, whereas protons H^C–H^G in the ligands that are coordinated to the Ln ion are in the region of $\theta > 54.7^\circ$. In the cases where Ln = Tb, Dy, and Ho, the sign of the shifts in the region of $\theta > 54.7^\circ$ is negative. This observation means that the value of D in eq 2 is positive for the three cases, indicating the presence of a uniaxial magnetic anisotropy along the C_4 -axis. In the cases where Ln = Er, Tm, and Yb, the signs of the

TABLE 3: Ratio of $\Delta\delta$ to $\Delta\delta(\text{H}^C)$ for [Y, Ln], [Ln, Y], and [Ln, Ln]

	H ^A	H ^B	H ^C	H ^D	H ^E	H ^F	H ^G
[Y, Tb] ^a	-0.21	-0.02	1	0.54	1.00	0.47	0.34
[Y, Dy] ^a	-0.22	-0.02	1	0.53	1.03	0.48	0.34
[Y, Ho] ^a	-0.21	-0.02	1	0.52	1.04	0.48	0.35
[Y, Er] ^a	-0.22	-0.03	1	0.56	1.03	0.48	0.35
[Y, Tm] ^a	-0.21	-0.02	1	0.55	1.05	0.49	0.36
[Y, Yb] ^a	-0.26	-0.05	1	0.56	1.13	0.54	0.39
Model 1 ^b	-0.267 ^a	-0.081 ^a	1	0.555 ^a	0.823 ^a	0.455	0.243
Model 2 ^c	-0.218	-0.023	1	0.555	0.982	0.522	0.329
[Tb, Y]	0.95	0.50	1	0.54	-0.20	0.08	-0.03
[Dy, Y]	1.00	0.52	1	0.54	-0.21	0.08	-0.03
[Ho, Y]	0.98	0.54	1	0.52	-0.20	0.08	-0.03
[Er, Y]	0.97	0.46	1	0.56	-0.20	0.08	-0.03
[Tm, Y]	0.98	0.49	1	0.55	-0.20	0.08	-0.03
[Yb, Y]	1.07	0.50	1	0.56	-0.28	0.06	-0.04
Model 1 ^b	0.823	0.404	1	0.555	-0.267	0.027	-0.101
Model 2 ^c	0.982	0.508	1	0.555	-0.218	0.089	-0.057
[Tb, Tb]	0.39	0.25	1	0.54	0.40	0.28	0.16
[Dy, Dy]	0.40	0.25	1	0.53	0.40	0.28	0.15
[Ho, Ho]	0.38	0.26	1	0.51	0.39	0.27	0.16
[Er, Er]	0.39	0.23	1	0.56	0.38	0.27	0.16
[Tm, Tm]	0.39	0.23	1	0.55	0.41	0.28	0.16
[Yb, Yb]	0.39	0.22	1	0.56	0.43	0.30	0.17

^a Data from ref 12. ^b The relative intensities of the geometric factor $[3(\cos^2\theta) - 1]/(2R^3)$ in Model 1. ^c The relative intensities of the geometric factor $[3(\cos^2\theta) - 1]/(2R^3)$ in Model 2 with $\varphi = 8^\circ$.

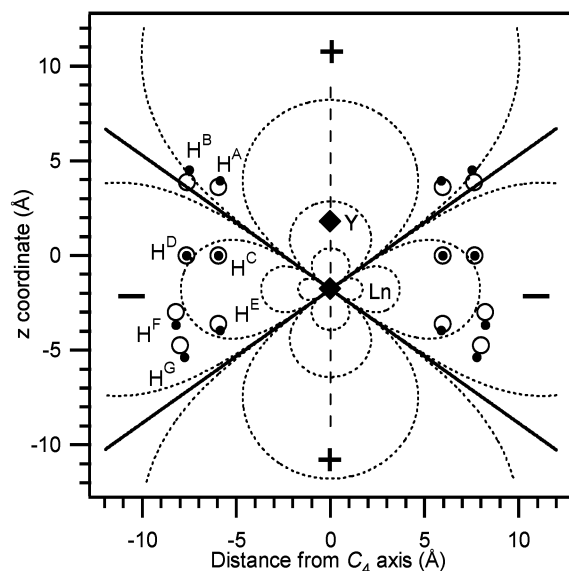


Figure 3. Isointensity plot of the magnetic-dipolar term in the NMR paramagnetic shifts in [Y, Ln] with Ln = Tb, Dy, or Ho. The signs are inverted for the case Ln = Er, Tm, and Yb. Solid lines represent the zero level. Dots and open circles represent the positions of the protons in Models 1 and 2, respectively. The horizontal coordinate for each proton refers to its distance from the C₄-axis.

shifts are reversed and D is negative, which indicates that the magnetization easy axis lies in the x - y plane.

In [Ln, Y] complexes, the center of the contours is moved to site 1 (see Figure 4). Accordingly, H^A–H^D in the Pc ligands that are coordinated to the Ln ion enter the region of $\theta > 54.7^\circ$, and H^E in Pc* far from the Ln ion lies in the region of $|\theta| < 54.7^\circ$. H^F and H^G of $-\text{OCH}_2-$ fall separately into the two regions. The observations in Table 2 are again consistent with the figure, which indicates that the observed $\Delta\delta$ values in the [Ln, Y] complexes have a magnetic-dipolar nature.

Prediction of Dipolar Terms Using Molecular Geometry Obtained by a DFT Calculation. Because the factor D in eq

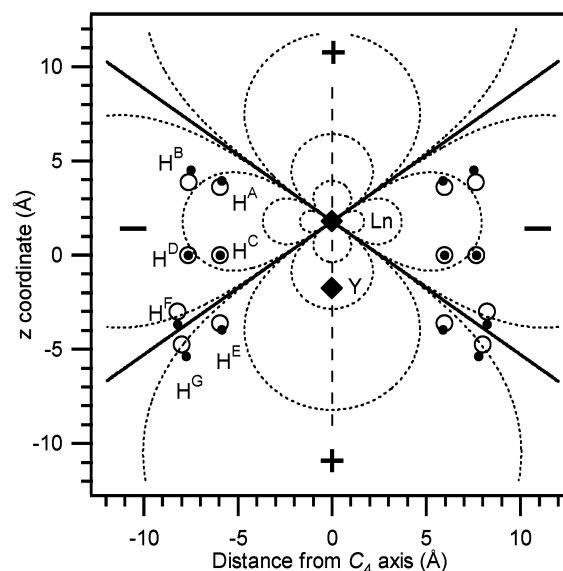


Figure 4. Isointensity plot of the magnetic-dipolar term in the NMR paramagnetic shifts in [Ln, Y] with Ln = Tb, Dy, or Ho. The signs are inverted for the case Ln = Er, Tm, or Yb. Solid lines represent the zero level. Dots and open circles represent the positions of the protons in Models 1 and 2, respectively.

TABLE 4: D Values, as Defined in eq 2^a

Ln	D value ($\times 10^{-26}$ emu) ^a	
	[Y, Ln]	[Ln, Y]
Tb	4.74	4.94
Dy	2.35	2.44
Ho	0.84	0.86
Er	-1.03	-1.10
Tm	-1.40	-1.44
Yb	-0.15	-0.15

^a The values were calculated with the geometric coordinates of H^C in the DFT models ($\cos \theta = 0.287$, $R = 6.21$ Å).

1 is constant for any atom in a molecule, the ratio of dipolar terms on two arbitrary atoms is determined solely by their spatial positions. If accurate positions of the atoms are known, one can determine the ratios using eq 1. Table 3 shows the theoretical values for the ratios using the two model geometric structures, namely Models 1 and 2. When Model 1 is used, the agreements of the theoretical values in the outer Pc and Pc* with the observed values are poor, although that of H^D on the center Pc is reasonably good. This is most likely due to the poor prediction of the deviation of planarity of the outer Pc ligands, because of the limited size of the basis set used in the DFT calculation.

To see if a moderate modification of the DFT structure can correct the disagreements, we calculated the dipolar terms using Model 2 with a varying angle φ . In Table 3, the results obtained with $\varphi = 8^\circ$ are presented. The agreement has been significantly improved in both [Y, Ln] and [Ln, Y]. The bending of the isoindole moieties to this direction means recovery of the flatness of the greatest portion of the Pc ligands, except for the coordinating N atoms. This result indicates that the DFT calculation with the limited basis set excessively emphasized the deviation from the planarity of the Pc ligands.

Because it can be quite safely said that Model 2 is a reasonably accurate geometric structure, it is now possible to determine the D factor in eq 2. Table 4 shows the D values obtained by eq 1 using the observed $\Delta\delta$ values and the spatial coordinates of H^C. Each value in the table represents the degree of anisotropy of the magnetic susceptibility of a Ln ion in the ligand field of the Pc triple-decker structure at 30 °C. As

TABLE 5: Hypothetical Paramagnetic Shift at One Ln Site due to the Other Ln Site in [Ln, Ln]^a

	at site 1	at site 2
[Tb, Tb]	1040	1090
[Dy, Dy]	515	536
[Ho, Ho]	186	189
[Er, Er]	-226	-241
[Tm, Tm]	-308	-317
[Yb, Yb]	-34	-32

^a Paramagnetic-shift values given in units of ppm.

discussed in the previous section, the D values are positive in the cases where Ln = Tb, Dy, and Ho but negative in the cases where Ln = Er, Tm, and Yb.

Additive Property of the $\Delta\delta$ Values in the Homodinuclear Complexes. Inspection of Table 2 reveals that each $\Delta\delta$ value of the homodinuclear [Ln, Ln] is expressed as the sum of the corresponding values of [Y, Ln] and [Ln, Y]. This observation indicates that the effects of the two Ln sites are basically independent of each other: the interaction between the paramagnetic Ln centers can be treated as negligible for the interpretation of ¹H NMR in the present case.

In a previous paper that studied the temperature dependence of the magnetic susceptibilities of [Ln, Ln] complexes,¹³ we have shown that the interaction between the two f-electronic systems in the dinuclear complexes essentially has a magnetic-dipolar nature and the contribution of the exchange interaction is negligible.

As an approximate picture of the effect of the magnetic-dipolar interaction between Ln ions, hypothetical paramagnetic shifts at an Ln site induced by the other Ln site were calculated by eq 1, using the values in Table 4 and the Y–Y distance in the DFT model ($R = 3.57 \text{ \AA}$). The results are shown in Table 5. The $\Delta\delta(\text{Ln})$ values represent the ratio of the averaged induced magnetic field at a position relative to the applied external magnetic field. The table shows that even the largest value of $\Delta\delta(\text{Ln})$ in the Ln = Tb case is 1×10^{-3} , meaning that the magnetic field to which a Ln ion is subjected is changed only by 0.1% at the maximum by the presence of another Ln ion. The small values indicate that the interaction between f-electronic systems in the homodinuclear complexes can be neglected for the discussions on the NMR signals in solution at room temperature.

From these observations, an important deduction is drawn for the general cases in which the two Ln ions are different. The paramagnetic shift of a proton in heterodinuclear complexes with two different heavy lanthanide ions, i.e., [Ln, Ln'] (Ln \neq Ln'), can be found by adding the corresponding values of [Ln, Y] and [Y, Ln'].

Why are All the Signs of the $\Delta\delta$ Values in a [Ln, Ln] Complex the Same? Another interesting point about [Ln, Ln] shown in Table 2 is that the signs of the $\Delta\delta$ values are all the same in a homodinuclear complex. This observation can be explained graphically by Figure 5. Superposition of the dipolar-term contributions from the two Ln ions yields the contour map for the dinuclear complexes. It is seen that all the protons lie in the same region, which is approximately the sum of the region defined as $\theta > 54.7^\circ$ for site 1 and that defined for site 2.

Conclusions

The stepwise analysis of the origin of the ¹H NMR paramagnetic shifts in the homodinuclear lanthanide complexes has shown the vital importance of the separation of the effects of the two paramagnetic centers. The relative $\Delta\delta$ values of the

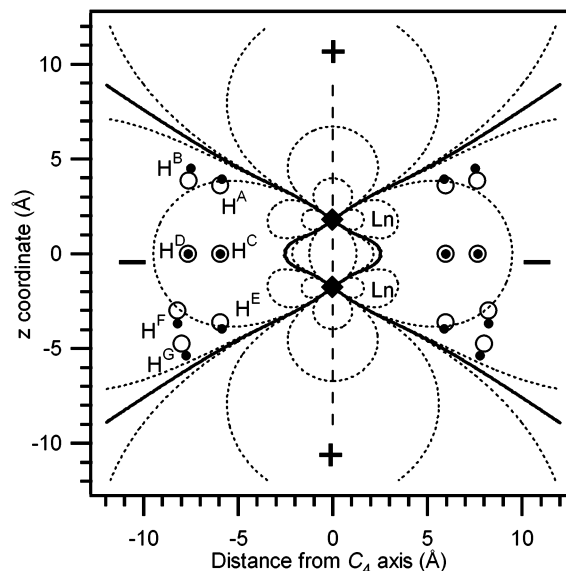


Figure 5. Isointensity plot of the magnetic-dipolar term in the NMR paramagnetic shifts in [Ln, Ln] with Ln = Tb, Dy, or Ho. The D values of the two Ln ions were assumed to be the same. The signs are inverted for the case with Ln = Er, Tm, or Yb. Solid lines represent the zero level. Dots and open circles represent the positions of the protons in Models 1 and 2, respectively.

protons in PcYpLnPc^* ([Y, Ln]) and PcLnPcYp^* ([Ln, Y]), where Pc is the dianion of phthalocyanine and Pc^* is the dianion of 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine, have been reproduced solely by the magnetic-dipolar term, using an appropriate geometric structure of the complexes. The $\Delta\delta$ values in [Ln, Ln] have been shown to be the sum of those of [Y, Ln] and [Ln, Y]. This observation indicates that the contributions of the two Ln sites are essentially independent from each other. The additive property of the paramagnetic shift values is explained by the small interaction between f-electronic systems in [Ln, Ln], because of its magnetic-dipolar nature. The signs of the paramagnetic shifts in [Ln, Ln] were all the same in one complex, because the positions of the protons lie in the same region in the contour map of the value of $\Delta\delta$.

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